Naval Research Laboratory

Washington, DC 20375-5320

AD-A278 838

Report on the Use of X-ray Fluorescence as a Trace Metal Sensor for the Cone Penetrometer

W. T. ELAM

Dynamics of Solids Branch
Condensed Matter and Radiation Sciences Division

J. V. GILFRICH

SAF, Inc.
Landover, MD

MAY 0 4 1994

February 28, 1994

94-13228

94 5 02 096

REPORT DOCUMENTATION PAGE

1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE February 28, 1994	3. REPORT TYPE AND DATES COVERED NRL Memorandum Report 1 June - 30 Sept. 1993

4. TITLE AND SUBTITLE

Report on the Use of X-ray Fluorescence as a Trace Metal Sensor for the Cone Penetrometer

5. FUNDING NUMBERS

6. AUTHOR(S)

W. T. Elam and J. V. Gilfrich*

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Naval Research Laboratory
Washington, DC 20375-5320

8. PERFORMING ORGANIZATION REPORT NUMBER

NRL/MR/6685--94-7420

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Naval Command, Control, & Ocean Surveillance Center
RDT&E Division
San Diego, CA 92152-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

*SAF, Inc., Landover, MD

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

This report addresses two sets of issues concerning the use of x-ray fluorescence as a sensor technology for the cone penetrometer. The first group concerns the applicability of XRF to this application, and includes investigation of detection limits and matrix effects. The second group is engineering issues involved with constructing a spectrometer within the physical constraints of the penetrometer.

14. SUBJECT TERMS

Metals	Sensor
X-ray absorption	Environmental
Penetrometer	

15. NUMBER OF PAGES

23

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL

CONTENTS

Executive Summary

This report addresses two sets of issues concerning the use of x-ray fluorescence as a sensor technology for the cone penetrometer. The first group concerns the applicability of XRF to this application, and includes investigation of detection limits and matrix effects. The second group is engineering issues involved with constructing a spectrometer within the physical constraints of the penetrometer. This executive summary presents the major results of the report in outline form.

Matrix effects
    Matrix effects not important for qualitative analysis
        Soils transmit x-rays at line energies for all metals above Ti
        Lines are well separated in x-ray energy
        Amounts can be determined within a factor of 2 w/o correction
    Accuracy of quantitative analysis depends on the standards used
        For standards with dissimilar matrix (ie - pure metals or oxides)
            matrix effects are large (2x)
            they can be corrected, but accuracy is limited to 10% to 50%
        For standards with similar matrix (ie - soils, SiO_2, etc.)
            matrix effects are much smaller (less than 50%)
            results are less sensitive to correction, giving better accuracy
            results can be corrected to better than 10% for known matrix

Detection limits
    Numerical detection limits are presented in Table I for a composite list of analytes
    The limits are adequate for solid materials (ie - solid hazardous waste determination)
    Not adequate for drinking water (100 to 1000 x too high)
    Limited by detector count rate and signal/background ratio
    The detection limits can be improved by increasing the detector count rate (several methods are proposed)

Engineering issues
    The x-ray source is straightforward
    There are several choices for an x-ray detector
        The most favorable choice is mercuric iodide, which operates at ambient temperature and pressure, but which may not yet have adequate energy resolution
        The second choice is an electrically cooled lithium-drifted silicon element, which requires a vacuum environment but which is well established and readily available commercially
    Boron carbide will make an acceptable window which will stand the expected pressures and transmit x-rays for all elements above Ti

Introduction

The cone penetrometer is a well-established method for exploring soil types whereby a small-diameter pipe with a hardened cone tip is pushed hydraulically into the ground on an extendible pipe. Measurements of sliding friction and penetration resistance provide information about the soil type. The Navy and Army have added down-bore optical spectroscopy to the penetrometer using fiber optics. This allows the penetrometer to be used to detect organic contaminants in the soil as it is pushed down. This system minimizes soil excavation, provides real-time information, and dramatically reduces environmental analysis costs. This report is a preliminary investigation on development of a new sensor for the penetrometer head to detect metals via x-ray fluorescence.

X-ray fluorescence (XRF) is a well-established, non-destructive method of determining elemental concentrations at ppm levels in complex samples. It can operate in atmosphere with no sample preparation, and provides accuracies of 1% or better under optimum conditions. It is currently used as an analysis method for samples obtained from hazardous waste sites both in the laboratory and with portable equipment on-site. Its characteristics are ideally suited to field analysis, and NRL has developed analyzers for real-time measurements on power plant stacks and remote air sampling stations[1].

The state of the art in x-ray fluorescence spectroscopy will allow the construction of a spectrometer which will meet the size restrictions imposed by the pipe diameter for the cone penetrometer. Such a device would allow sampling of atomic element concentrations at the ppm level during descent of the penetrometer. High sensitivities (at or below ppm levels) could be achieved while the head is stationary for several minutes. Continuous monitoring at lower sensitivity is possible depending on descent rates, contaminant concentration, and soil type.

The development of new miniaturized sensors to fit behind the cone (maximum diameter 2 inches) provides the greatest potential for increasing the utility of this system. An x-ray fluorescence (XRF) sensor will extend the range of contaminants which can be detected with the penetrometer from the organics mentioned above to include trace metals and possibly other important elements, such as chlorine and sulfur.

This report is aimed at understanding the issues involved in development of an X-ray fluorescence sensor to be deployed on the cone penetrometer. A short description of x-ray fluorescence will be given, followed by a conceptual description of the sensor. Issues specific to the penetrometer will be enumerated and discussed. Both experimental measurements and calculations have been performed to demonstrate the capabilities and limitations of XRF as well as to confirm the possibility of designing an adequate sensor for the cone penetrometer. Lastly, some suggestions for further work to better define the parameters for a prototype sensor are given.

X-ray Fluorescence

X-ray fluorescence operates by detecting characteristic x-rays emitted by the atoms in a sample. The process is diagrammed in Figure 1 where the physical layout of the apparatus is shown on the left. An x-ray source bombards a sample with incident x-rays, where the atoms are excited and emit fluorescence x-rays. The fluorescence x-rays are detected as shown at the bottom of the figure. The atomic process which produces the fluorescence x-rays is illustrated in the box at the right of the figure. The diagram shows a typical set of energy levels for the electrons in an atom in the sample. Energy is plotted vertically and the various interactions are separated horizontally. An incident x-ray excites an electron from a core level near the center of the atom to an empty state above the atomic states. The incident x-ray can have any energy which is greater than the binding energy of the core electron. The empty core state is re-filled by an electron from within the atom, producing a fluorescence x-ray. Since the electron energy states producing the fluorescence x-ray are entirely within the atom, the x-ray is produced with a constant and well-known energy (different for each type of atom). The excitation of core states (unlike the valence states used in atomic and optical spectroscopy) causes the fluorescence x-rays to have relatively high energies and thus be mostly independent of the chemical state of the atoms. The relatively high energy of the x-rays makes them penetrate any type of matter for distances of several microns to several millimeters, regardless of optical transparency. Any type of atom with sufficiently energetic core levels can be detected in any matrix. Generally, elements with atomic numbers greater than 19 (potassium) can be detected under ambient conditions, with elements down to 6 (carbon) detectable with vacuum sample chambers.
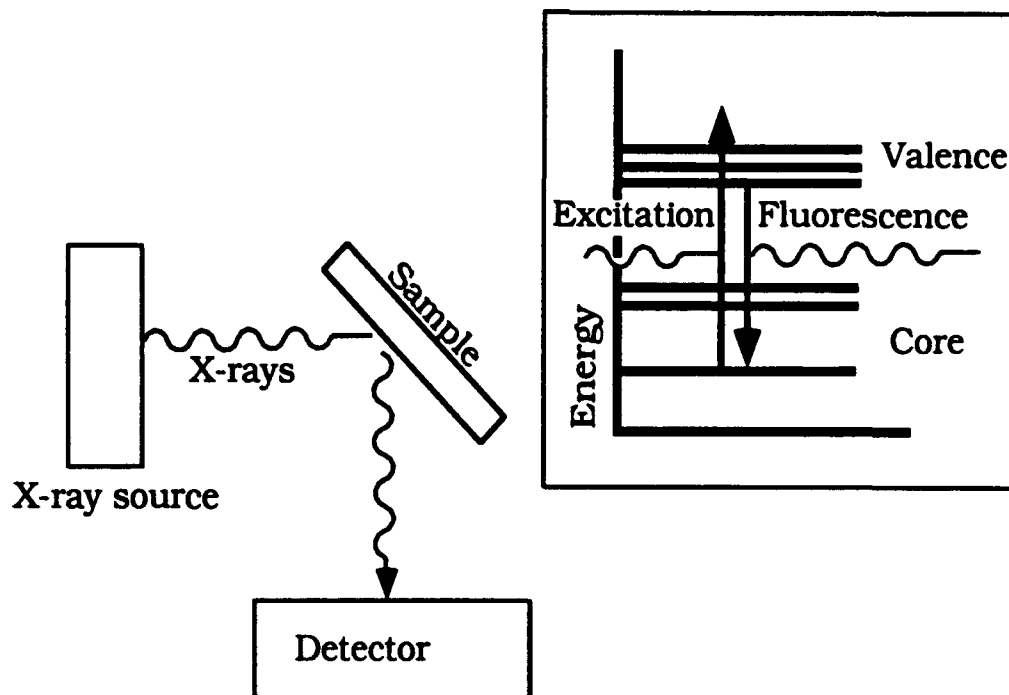
2

Figure 1 - Diagram of physical processes in x-ray fluorescence. The layout of the apparatus is shown on the left. The box on the right sketches the electron energy levels in a typical atom and the transitions which produce the fluorescence x-rays.

In general , the instrumentation used for x-ray fluorescence analysis can be divided into two broad classes, described as wavelength dispersive and energy dispersive. Wavelength dispersion ordinarily requires high power and large laboratory equipment, while energy dispersion can use much lower power and can be made more compact. Thus, virtually all portable x-ray fluorescence instruments are of the energy dispersive type, and the application to the penetrometer must take advantage of new developments in that technology.

The detection limits for a particular element depend on the efficiency with which it produces fluorescence x-rays (a fundamental physical property of the atom), the transmission of x-rays by the matrix and the apparatus (including the medium in the beam path and geometric effects), the x-ray source intensity, and the detector efficiency. Current energy dispersive instruments are generally limited by saturation of the detector, making further increases in source intensity impractical. This limits detection to greater than a few parts per million for metals in a typical matrix. Detection limits into the parts per billion range have been demonstrated under special conditions[2].

The sensitivity to a particular element depends on the atomic properties mentioned above and the effect on the element's

fluorescence x-rays by the matrix. Since the matrix composition may not be well known, methods for compensating for matrix effects must use information from the XRF spectrum as much as possible. This includes the effects of the elements being measured by XRF, since they can affect the matrix absorption if concentrations are large. The scattering of the incident x-rays by the sample also produces a characteristic pattern which depends on the average atomic number and can be used to produce fairly accurate matrix corrections[3]. Accuracies of 1% or better are typical for analytical work with a full complement of carefully chosen standards[4].

XRF Sensor Concept

An XRF sensor capable of fitting within the pipe of the cone penetrometer would consist of a small commercial x-ray tube, collimating apertures and x-ray filter, one or more x-ray windows, and an energy dispersive detector. The x-ray tube would require a source of high voltage (approximately 50kV), which could be generated near the sensor or on the surface and carried by a cable. The power requirements are only a few watts and are easily handled. The detector will require a source of bias voltage (a few hundred volts) and a pre-amplifier to prepare the signal for transmission to the surface via coaxial cable.

X-ray tubes one inch in diameter are available from commercial suppliers. Such a tube would fit within the two inch penetrometer pipe easily, with room left for apertures, x-ray filters, and windows. The windows must transmit x-rays while withstanding the pressures from the soil depth and abrasion during descent. The next section covers the relevant requirements, calculations, and materials necessary for choosing a successful window. The detector is a solid state energy-dispersive detector. The traditional lithium-drifted silicon diode must be cooled to reduce the electronic noise and achieve sufficient resolution. An electrical Peltier cooler would be employed if uncooled detectors now available do not have sufficient energy resolution.

A conceptual layout of a sensor employing a one inch x-ray tube and a cooled Si(Li) detector is shown in Figure 2. In front of the tube is an aperture to block the x-rays from the source from directly entering the detector. The detector is below the tube in the pipe, and is positioned to accept x-rays which enter through the windows. There are four windows approximately 1/4 inch in diameter each. The narrow confines of the penetrometer pipe force the detector close to the windows, which has the advantage that a small detector still accepts an appreciable solid angle from the excited volume of soil.

Room for pipe walls of one-quarter inch is included, as is a shielded passage for cables to pass through the sensor. The direct x-ray flux from the tube would be enough to eventually darken optical fibers, but the steel walls will adequately shield the fibers and other cables.
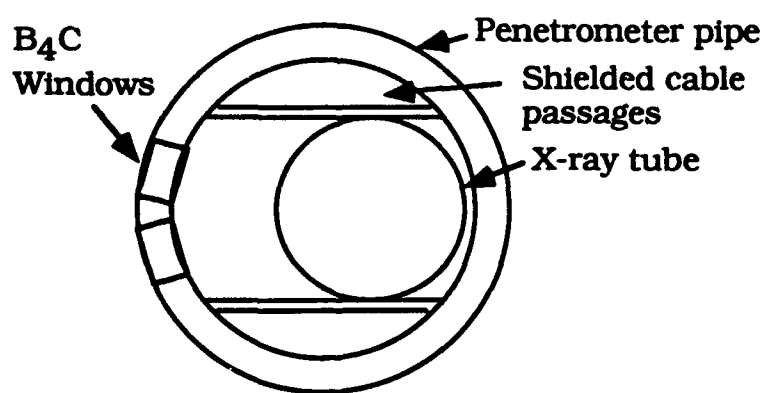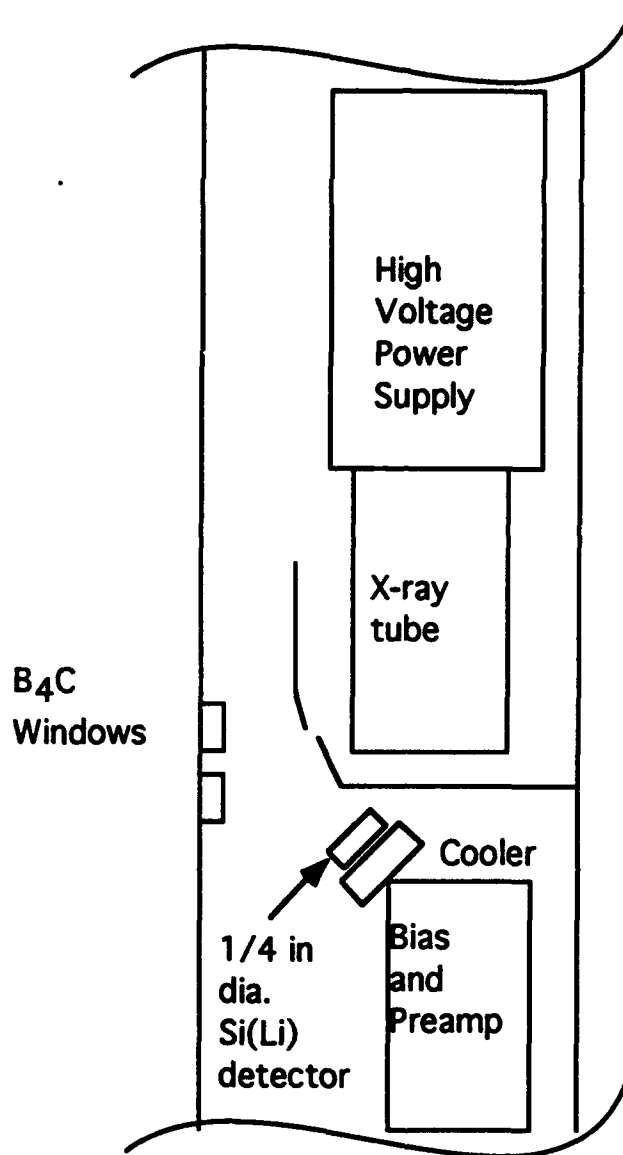
High
Voltage
Power
Supply

X-ray
tube

B$_4$C
Windows

Cooler

1/4 in
dia.
Si(Li)
detector

Bias
and
Preamp

B$_4$C
Windows

Penetrometer pipe

Shielded cable
passages

X-ray tube

Figure 2

Issues for XRF Sensor

Experimental Investigation

To perform a proof-of-principle experiment and to investigate the detection limits and matrix effects expected for an XRF sensor on the cone penetrometer, a laboratory mock-up of the sensor was constructed. An available laboratory x-ray tube and detector were used; the x-ray tube was operated at very low power and the detector was an electrically cooled model with a small active area. The source-to-sample and sample-to-detector distances were kept short (though still somewhat longer than possible in the penetrometer) and an aperture and incident x-ray filter similar to those intended for the penetrometer sensor were used.

The source was a spectroscopic x-ray tube, Phillips FAAQ 60/3.5, with a molybdenum target and a spot size of 5.5 x 8 mm. Molybdenum is chosen since its K alpha line emission at 17.4 keV excites most of the elements of interest but is not too far above the transition metal edges, such as titanium and iron. It was operated at 35 kilovolts and 0.4 milliampere (14 watts). An aperture of 2.5 millimeters and an x-ray filter of 0.052 mm thick molybdenum sheet were placed between the source and the sample. The detector was a Peltier cooled lithium-drifted silicon diode, Kevex "Super Dry", which has a 30 mm^2 active area and an energy resolution of about 190 eV at the count rates used here. Its associated amplifier was set to put out pulses about 16 microseconds wide, limiting the detector to about 10,000 counts per second.

Spectra were collected on a series of soil samples from the National Institute of Standards and Technology (NIST), Standard Reference Materials 2709, 2711, and 2710. The are typical western soils with baseline, moderately elevated, and highly elevated levels of metal contamination, respectively. The spectrum from the baseline soil is shown in Figure 3 for a counting time of 100 seconds. The element responsible for each line is identified, as are the lines from the incident radiation scattered by the sample. The soils were held in one-eighth inch thick Lucite holders, one inch in diameter. A spectrum taken on an empty holder under the same conditions showed no discernible peaks above the background. The area under each peak in the spectrum was obtained by integrating each peak over 1.2 times its full width at half maximum and subtracting a background found by linearly interpolating between points just past the skirts of the peak. This peak area (net counts per 100 seconds) was used in all subsequent analysis.

6

SRM 2709
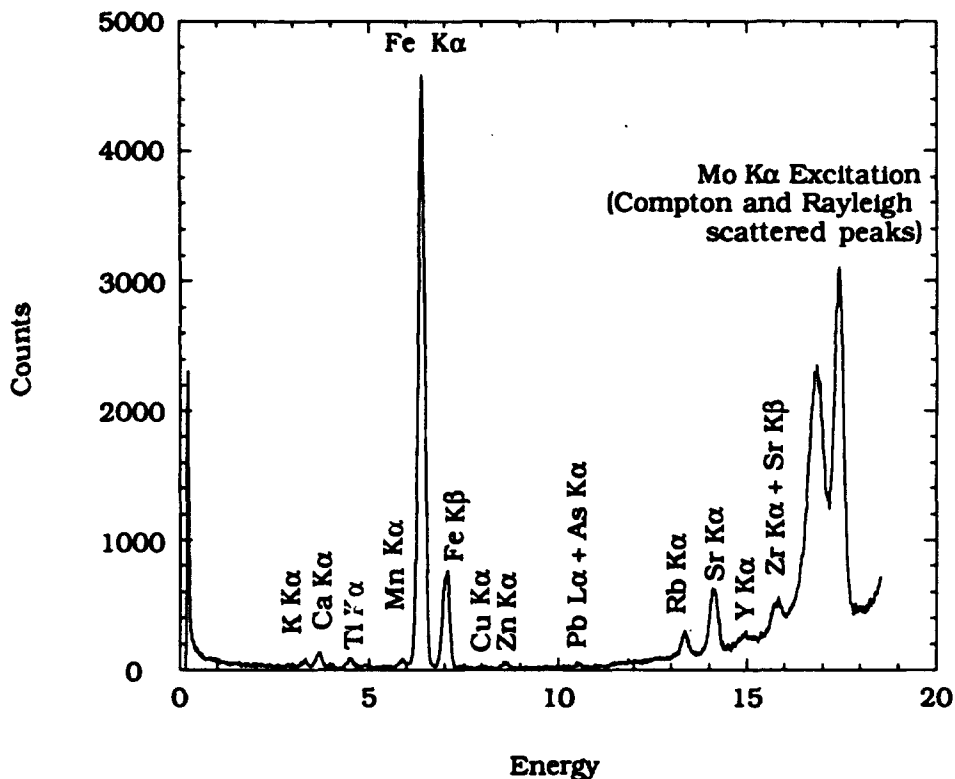## San Joaquin Soil with Baseline Trace Element Conc.

Figure 3

Detection Limits

Detection limits were calculated using the spectra for all three soils. The net counts as described above were divided by the certified concentrations, as contained in the NIST Certificates of Analysis, to obtain a sensitivity in counts per 100 seconds per ppm. This was then divided by 3 times the square root of the background under the corresponding peak to obtain the three sigma detection limit.

The detection limits for a list of metals are given in Table I. This list is combined from several sources[5]. The detection limits measured using the NIST Standard Reference Materials are shown together with those obtained from the literature[6]. Also listed are the x-ray energies for each of the metals and the toxicity levels from the regulatory definition for solid hazardous wastes[7]. As can be seen, the detection limits currently achievable are near or below the required levels for most metals. For example, our results for lead are within a factor of two of the regulatory limit for solid waste. Since the NIST soils did not contain all of the metals which might be of interest because of their toxicity, values from the literature obtained using commercial instrumentation were included in the table. Our

experimental apparatus gives results which are at or near the literature values over most of the energy range. It should be noted that some commercial instruments require slight re-configuration to optimize them for detecting different elements, while our experimental mock-up operates in a single configuration. The slightly poorer detection limits for elements with lower x-ray energies are due to our use of molybdenum excitation, which is optimized for the heavier (and more toxic) elements rather than for the lighter elements (like iron and manganese). The high detection limit for the barium K_α line is because it is excited only by the continuum radiation above the barium K edge at 33 keV. The detection limits demonstrated by our experimental setup may improve slightly in the actual penetrometer sensor, since it will have even closer coupling between the source, sample, and detector. The table shows that for all elements listed in the solid waste regulation the XRF detection limits are within a factor of four of the regulatory limits, except for mercury. While the extremely low regulatory limit for mercury may be difficult to reach, it (as well as all of the elements listed here) can be detected and quantified at levels well below those typically encountered at contaminated sites.

While the detection limits demonstrated here are adequate for soils and other solid wastes which the penetrometer will typically analyze, it should be noted that the toxicity levels for drinking water are one thousand times lower than the levels for solid waste. These much lower levels provide a more stringent criteria which might be used in some regulatory or public relations matters. It is worth considering possible ways to improve the detection limits. X-ray fluorescence is not currently capable of detecting metals at the concentrations important for drinking water analysis in reasonable counting times without some chemical concentration. The limitation is in the count rate of the detector, which must process one x-ray photon at a time to achieve energy discrimination. The detector is easily saturated by the scattered x-rays from the majority components in the sample at very low contaminant concentrations. This may be overcome by using energy discrimination methods after the sample but before the detector to reduce the scattered radiation[2], or by improved pulse processing after the detector to increase its count rate. If the detector count rate can be improved, the x-ray source could be easily increased in intensity to improve the detection limits or provide shorter counting times.

Table I. Combined Pollutant List with Detection Limits and Solid Waste Toxicity Levels

Element	X-ray Energy (K_α lines)*	Detection Limit (ppm) NRL	Ref. 6	RCRA Toxicity Level
Antimony	26.3		5	
Arsenic	10.5		8	5
Barium	32.2	87		100
Cadmium	23.1		4	1
Chromium	5.41		16	5
Cobalt	6.93			
Copper	8.04	12	16	
Iron	6.40	79	19	
Lead	10.5 (L_α)	10	6	5
Manganese	5.89	120	21	
Mercury	9.98 (L_α)			0.2
Nickel	7.47		14	
Selenium	11.2			1
Silver	22.1	21	8	5
Thallium	10.3			
Vanadium	4.95			
Zinc	8.63	10	11	

* except as indicated

Matrix effects

The other uncertainty in the use of x-ray fluorescence with the cone penetrometer is the effect of various soil matrices on the reliability and accuracy of analysis. Soils typically consist of a mixture of silicon dioxide (sand) and various minerals together with organic material. The sand and organic materials have low average atomic number and thus transmit x-rays of the requisite energy relatively well. Fluorescence x-rays from copper, for instance, will travel more than a millimeter in organic material and one-tenth millimeter in silicon dioxide. Other minerals in soils can reduce this range somewhat, but soils still provide adequate transmission of x-rays to allow easy detection of most metals via x-ray fluorescence. More importantly, the soil matrix does not effect the energy of the fluorescence x-rays, and thus the line position in the spectrum. Specific elements can be detected and identified unambiguously regardless of the matrix in

which they are found - sand, clay, porous rock, or even water. Moreover, the amounts of the metals present can be determined within a factor of two without any correction for the type of matrix, within broad limits. As long as the concentration of metals is below several percent, the matrix effects are dominated by the soil, whose maximum variations in x-ray absorption are not large compared to other matrices. In short, matrix effects are not important for qualitative analysis of metals in soils.

Quantitative analysis, however, must take into account the absorption of the incident and fluorescence x-rays in the matrix (including the absorption of the various trace elements). This is particularly true if standards with a dissimilar matrix (such as pure oxides or metals) are used for calibration. Matrix effects can be larger than a factor of two in this case. Corrections can be made by calculating the x-ray absorption using fundamental parameters, but accuracy is limited to 10 to 50% by uncertainties in these parameters. When metals at concentrations similar to the unknown in a similar matrix are used, the matrix corrections are much smaller; accuracies better than 50% can usually be obtained without any matrix correction. Since the correction is smaller, the accuracy is less sensitive to errors in the parameters and to uncertainties in the matrix composition if corrections are made. The results can be corrected to achieve accuracies better than 10% if the matrix is known. The effective atomic number, and thus the x-ray absorption, of the matrix can be obtained from the intensity ratio of the Compton (inelastic) to Rayleigh (elastic) scattering of the intensity radiation by the matrix. These two peaks are labeled in the spectra shown in Figure 3 and in Figure 4.

SRM 2711
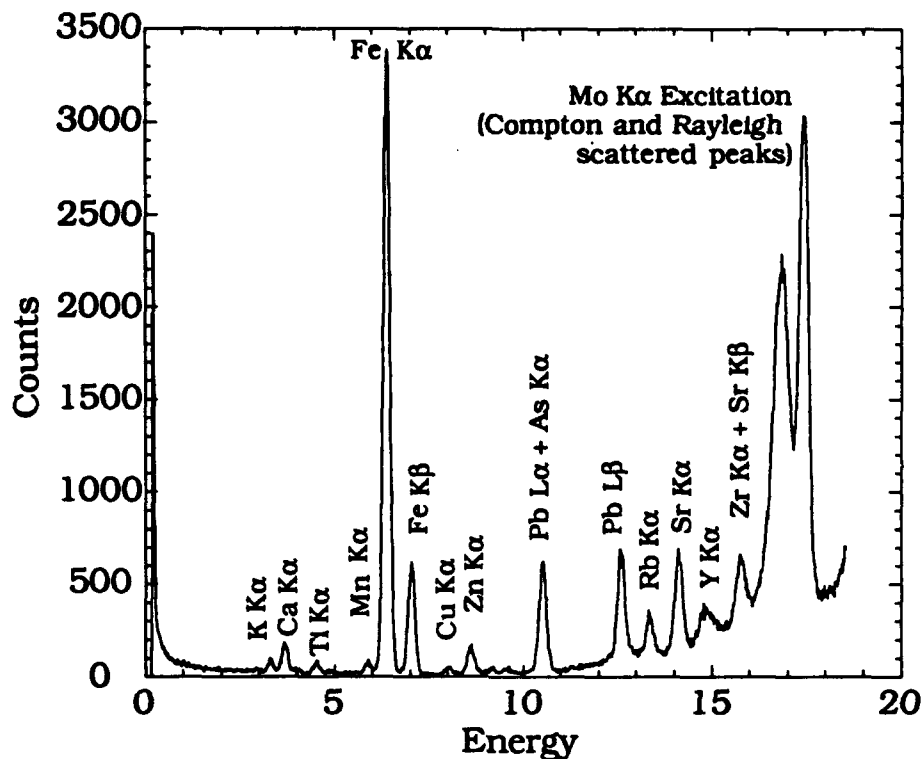## Montana Soil with Moderately Elevated Trace Element Conc.

Figure 4

To give a concrete example, the spectra shown in Figure 4 was analyzed quantitatively and compared to the certified values of metals present as determined by NIST. The results were calculated using both a very different matrix (a set of pure metal oxides) and similar matrices (the other two Standard Reference Material soils) or both. Values without any correction were calculated by taking the ratio of net counts for the peak of a given element in the standard vs. the "unknown" multiplied by the concentration in the standard. Matrix effects were corrected by using the fundamental parameter calculation program NRLXRF[8]. The results are presented in Table II. As can be seen, the corrected results for similar matrices agree with the certified values to within 10%, and the uncorrected values to within about 50%. For dissimilar matrices without correction the error for lead is a factor of ten. A more visual comparison is given in Figure 5, where the corrected measured values are compared graphically with the certified values.
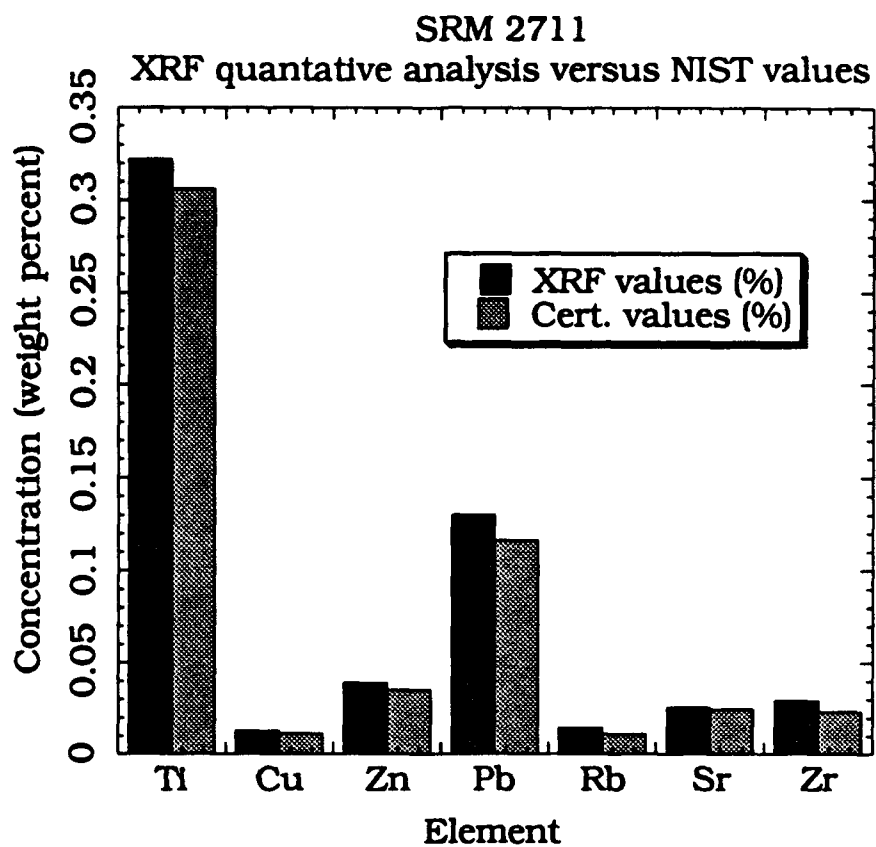
SRM 2711
XRF quantative analysis versus NIST values

Figure 5

Table II. Quantitative Results for Soil Analysis via XRF

Standards with similar matrix

Element	NIST value	without corr.	with corr.
copper	.011	.009	.012
zinc	.035	.051	.039
lead	.116	.132	.130
rubidium	.011	.013	.014
strontium	.024	.034	.025

Standards with dissimilar matrix

Element	NIST value	without corr.	with corr.
copper	.011	.021	.01
zinc	.035	.078	.04
lead	.116	1.26	.189
rubidium	.011	.098	.017
strontium	.024	.193	.045

Sensor Engineering

Source

Several engineering issues must be considered when designing an x-ray fluorescence sensor for the cone penetrometer which do not relate directly to spectroscopic requirements. The first of these center around the x-ray source. A conventional x-ray tube operates by emitting electrons from a filament and accelerating them into a target. X-rays are produced when the electrons strike the target. The energy of the x-rays is dominated by the energy of the electrons and the material of the target. The majority of the x-rays will be emitted at the fluorescence x-ray energy of the target material. The electrons must have sufficient energy to excite the fluorescence energy levels of the target. Higher electron energies, unlike x-rays, are more efficient at excitation. Consequently, an electron acceleration voltage in the range of about 50 kilovolts is preferred. The currents are modest; it is estimated that less than one milliampere will be required given the tight geometry in the penetrometer. This gives a total power of 50 watts.

Commercial x-ray tubes of approximately one inch diameter are available. This is near the upper limit of what will fit in the pipe, but a commercial tube will be much cheaper than a custom tube. Adapting the geometry to fit such a tube, together with its high voltage connectors, will produce considerable cost savings. It is estimated

that the x-ray tube will be the second most expensive component (after the detector), in the range of several thousand dollars. At the low power levels anticipated, the tube should be able to operate without cooling or by using the pipe as a heat sink.

A power supply to meet the high voltage requirements is easily constructed, but two constraints unique to the penetrometer must be considered. The small diameter of the pipe implies that both the configuration and the insulating material must be carefully chosen to avoid breakdown. Attention to keeping moisture out of the high voltage connections has proven most often to be a source of problems. Two options are available. A conventional commercial power supply can be located on the surface and the voltage led to the sensor via a cable passing down the pipe. Cables to handle 50kV are in routine use, but they are typically more than one inch in diameter. A special cable would have to be purchased, which would be expensive given the length (typically 50 meters). An alternative is to locate the power supply near the tube. Such a miniature high voltage supply should be straightforward to construct given the modest power requirements and the routine availability of switching power supply components. It has the advantage of reducing the need for high voltage connections as well as eliminating the cable. It would increase the cost of the sensor if it is lost, but might substantially reduce the cost and increase the reliability of the total instrument.

Detector

Several choices are available for the detector. An energy dispersive detector is necessary, since energy selection via diffracting crystals (wavelength dispersion) is not practical in the available space. Among energy dispersive detectors the lithium-drifted silicon diode is the most widely used and best developed. It has an energy resolution of better than 150 eV and a count rate which can approach 30,000 counts per second. There is some trade off between resolution, determined by electronic noise in the diode, and count rate, determined by averaging time in the electronics. Silicon diodes are normally cooled to reduce the noise, with liquid nitrogen being the usual refrigerant. Since liquid nitrogen is impractical in many situations (including the penetrometer), detectors which are electrically cooled by Peltier coolers have been developed. Such detectors suffer slightly in energy resolution, since they are not as cold. The principal drawback to a cooled detector is that it must operate under very good vacuum.

Recently, detectors using a mercuric iodide crystal have been developed which operate at room temperature and ambient pressure (though they must be protected from humidity, etc.). These detectors do not yet achieve the energy resolution of silicon detectors, but they are within the range usable for XRF and have been included in commercial detectors. The energy resolution is typically slightly above 200 eV[9], adequate for most purposes. This represents the most promising choice for an XRF sensor for the penetrometer. However,

an electrically cooled Si(Li) detector could be used if the mercuric iodide detectors prove unsuitable.

Window

A window must be used to protect the x-ray source and detector from the dust, liquids, and abrasion to which the penetrometer is subjected during deployment. Such a window must be sufficiently transparent to x-rays while retaining sufficient strength to resist the forces of the soil on the sides of the pipe. X-ray transmissivity requires low atomic number materials, such as beryllium, boron, and carbon. Beryllium is the typical window material in x-ray tubes, but is not hard enough to resist abrasion by soils and is highly toxic. A graph of the x-ray transmissivity of several materials is shown in Figure 6. The graph is for a constant thickness of material rather than a constant strength. Thus diamond, which has a very high tensile strength, may be a better material than boron carbide when this parameter is taken into account. The expense and difficulty of obtaining diamond windows of appreciable size rules it out for now as a candidate. Developments in synthetic diamond growth may change this dramatically in the near future. For the present, boron carbide is the only hard, strong material which has sufficient x-ray transmissivity.
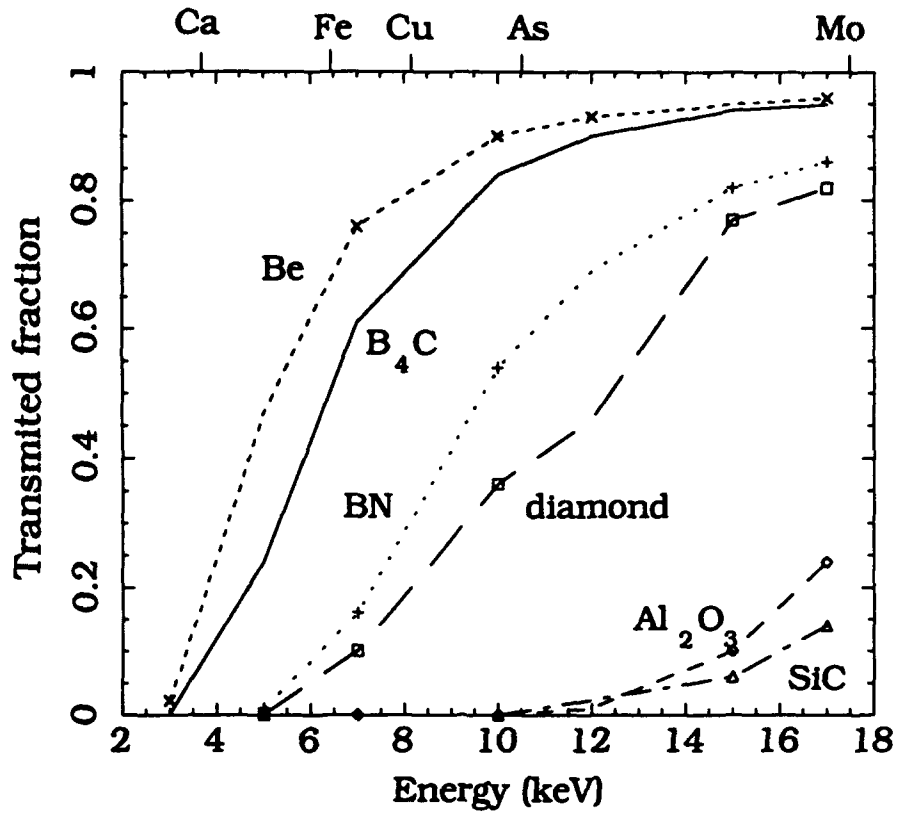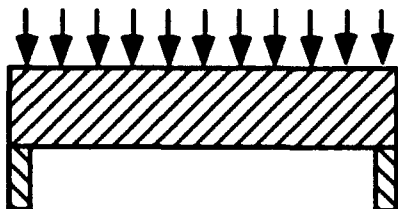
Absorption of 1 mm of material

Figure 6

The question then arises as the whether boron carbide has sufficient strength to withstand the expected forces during penetrometer deployment. The forces on a circular window under constant external pressure and shown below, together with the equation for the stress on the window material.

16

$$S = \frac{0.39\ W}{t^2}$$

Circular flat plate
Uniformly loaded
Supported around edges
Thin, small deflections
Poisson ratio near 3

S = maximum stress (psi)

W = total load (pounds)

t = thickness (inches)

The conditions listed in the figure are generally applicable to windows in the wall of the penetrometer. The range of pressures encountered in the penetrometer is 50 to 250 pounds per square inch (psi)[10]. For a window of 0.25 inch diameter and 0.040 inch thickness (the thickness used in the plot in Figure 6), and a load of 250 psi, the stress on the window material is 3200 psi. Boron carbide has a shear strength of 29,000 psi, giving almost a factor of ten margin. It should be noted, however, that occasional stresses much higher are encountered, especially if the penetrometer hits a rock during descent. The actual window thickness should be chosen to avoid an undue failure rate while allowing as much x-ray transmission as possible. Thicker windows can be offset somewhat by increasing the source intensity, but loss of sensitivity to the lower atomic number elements (like titanium) would be irrecoverable.

---

[1]J. V. Gilfrich and P. G. Burkhalter, "Portable Vacuum X-ray Spectrometer Instrument for On-Site Analysis of Airborne Particulate Sulfur and Other Elements", EPA-600/7-78-103, 1978.

[2]Boris Yokhin and Robert C. Tisdale, "High-sensitivity energy-dispersive XRF technology", American Laboratory 25 (Sept. 1993), pp 36H-36O.

[3]Kirk K. Nielson, "Matrix Corrections for Energy Dispersive X-ray Fluorescence Analysis of Environmental Samples with Coherent/Incoherent Scattered X-rays", Analytical Chemistry 49 (April 1977), pp 641-648.

[4]L. S. Birks, X-ray Spectrochemical Analysis, Interscience (New York, 1969), p 80.

[5]Hazardous metals contained in the "Definition of Hazardous Solid Waste" in 20CFR261, the EPA target analyte list, and the limits for drinking water in the Safe Drinking Water Act were combined to obtain this list.

[6]W. Watson, J. P. Walsh, and B. Glynn, "On-site X-ray Fluorescence Spectrometry Mapping of Metal Contaminants in Soils at Superfund Sites", American Laboratory 21, (July 1989), pp 60-68.

[7]20CFR261, which specifies the metal contaminants and lower limits which trigger the classification of solid waste as hazardous waste.

[8]J. W. Criss, L. S. Birks, and J. V. Gilfrich, "Versatile X-ray Analysis Program Combining Fundamental Parameters and Empirical Coefficients", Analytical Chemistry 50, (January 1978), pp 33-37.

[9]P. F. Buckens and R. S. Marano, "Thickness guaging of organic films on large plastic body parts with an XRF probe based on a room-temperature Mercuric iodide detector", 42nd Annual Denver Conference on Applications of X-ray Analysis, August 2-6, 1993, Denver, CO, paper # F32.

[10]Loads represent pressures measured by geotechnical sensors on the penetrometer and were obtained from the U. S. Army Waterways Experiment Station.